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The Effect of High Intensity Ultrasound on the Synthesis of Some Polyurethanes

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Abstract

High intensity ultrasound has been applied to the preparation of polyurethanes from a number of diisocyanates and diols. In all cases, the sonochemical reactions proceeded faster in the early stages and led to higher molecular weight polymers. The effect of changing the ultrasound intensity is discussed and some speculation as to the mechanism of the reaction enhancement is given.

Keywords: Sonochemistry; cavitation; polymerisation rates; polyurethanes; ultrasound.

Introduction

Polyurethanes are amongst the most widely applied polymers in use¹. Variation of the diisocyanates and diols used together with the inclusion of various chain extenders allows a huge range of properties to be achieved. One method of preparation is to form a low molecular weight “pre-polymer” which can then be processed into the final form. Alternatively, a “one-shot” reaction with all the components can be used, often used with a metal containing catalysts such as tin octanoate.

The use of high intensity ultrasound has become a useful tool in synthetic chemistry^{2,3}. Applying ultrasound – ‘sonication’ or ‘insonation’ - has also been found to affect the course of a series of polymerisation reactions^{4,5}. Most sonochemical effects can be attributed to cavitation⁶, the growth and explosive collapse of microscopic bubbles as the sound wave propagates through the fluid. This can result in extreme conditions of temperature (> 2000K) and pressure (>500 bar) on a microsecond timescale⁷. The motion of fluid around the bubbles is rapid resulting in very efficient mixing or the formation of jets of liquid against solid surfaces⁸. The rapid motion can result in effective shear degradation of polymer chains in the vicinity of cavitation bubbles⁹ as long as they are over a certain molecular weight.

In terms of polymer synthesis, the most studied reaction is that of radical polymerisation of vinyl monomers. Ultrasound can obviate the need for thermal initiators and hence can be applied at low temperatures. Some control over the molecular weight and polydispersity can be achieved^{10,11}.

Given the large number of industrially important polymers and plastics prepared *via* step-growth reactions, there have been few reports of the application of ultrasound in this area. Watanabe *et al.* applied ultrasound from a cleaning bath to the preparation of aromatic polyformals¹². Long¹³ described various reactors which incorporated ultrasonically vibrating walls and could be used for control of both when and where polymerization took place for several polyurethane systems and was especially useful for producing foams.

There has also been some interest in ring-opening reactions. For example, Stoessel¹⁴ has also reported the use of ultrasound at very high intensities to promote the polymerisation of small cyclic polycarbonate oligomers. The effect of ultrasound on the reaction of caprolactam to form Nylon-6 has been studied by Ragaini¹⁵ *et al.* who showed that ultrasound enhanced the ring opening allowing a single step polymerization. High molecular weight materials with narrower distributions were formed in shorter reaction times than when using the conventional process and sonication

allowed the polymerization to be run at lower temperatures than under conventional conditions. Other work in the area of ring opening reactions has involved the polymerization of cyclic siloxanes to silicone resins¹⁶.

This communication presents a preliminary investigation into the effect of ultrasound on the formation of polyurethanes. Polymerisation times and molecular weights have been measured for reaction of a range of diols and diisocyanates.

Experimental

Polymerisation methods: The diisocyanate and diol involved were weighed into the reaction vessel in a 1 : 1 molar ratio. In some reactions, 0.1 wt% of dibutyl tin dilaurate was added as a catalyst. Reactions were carried out on approximately 25 – 30 cm³ scale by stirring while being heated or by being insonated.

In preliminary experiments, the onset of polymerisation was detected by noting a significant increase in viscosity. The solidification of the mixture was also assessed visually. This was facilitated in the ultrasound experiments since the change in state of the reaction mixture caused a change to the pitch of the ultrasound horn which corresponded with solidification of the reaction.

Sonication techniques: The main source of ultrasound used was a Fisons 'Soniprep 150' sonic horn system operating at 23 kHz and used in the configuration shown in Figure 1. The transducer produces mechanical vibrations which are coupled into the solution via a 1 cm diameter titanium horn. Thermostating was achieved to ± 0.5 °C by circulating water through the jacket although this degree of control could not be achieved during some highly exothermic polymerisations. Sonication intensities were measured calorimetrically¹⁷. For comparison purposes, some reactions were carried out by immersing a beaker containing the reagents into a Ney 'Ultrasonik 300' ultrasonic cleaning bath.

Figure 1 near here

Materials: A number of diisocyanates were used. H₁₂MDI (4,4'-dicyclohexylmethane diisocyanate) and m-TMXDI (1,3-bis(isocyanato-1-methylethyl)benzene) were obtained from Bayer Ltd; IPDI (isophorone diisocyanate) was from Hüls; VM10 and MDI (4,4'-diphenylmethane diisocyanate) from ICI. The structures are shown in Scheme 1. Appropriate safety precautions were taken to minimise exposure to these compounds. The diol compounds were all obtained from Aldrich in the purest form

available. The water content was measured by the Karl-Fischer method to be less than 0.2 wt%. Solvents and other reagents used were of Reagent grade or better and were obtained from Aldrich Ltd.

Analytical methods: Infra-red spectra were recorded as films on NaCl plates using a Perkin-Elmer PE983 spectrometer. Molecular weights were estimated using a Gel Permeation Chromatograph operating at 80 °C in dimethyl formamide stabilised with LiBr at a flow rate of 1 cm³ min⁻¹. Calibration of the two 30 cm 'PL Gel' columns was performed with PEG / PEO standards (Polymer Laboratories Ltd). The values below are quoted as "PEO equivalent" molecular weights.

Results and Discussion

The initial phase of the work involved a determination of the potential utility of ultrasound by a survey of several diisocyanate/diol systems used in commercial polyurethane production. Polymers prepared from H₁₂MDI and 1,4-butane diol are used in surface coatings. Figure 2 shows the time taken for this system to form solid polymer under a variety of conditions. In each case, a brittle, transparent polymer was produced except for the catalysed reaction with the ultrasonic horn where some foaming was observed. There is a clear acceleration of the reaction under ultrasound in both catalysed and uncatalysed reactions. Note that this is not simply a temperature effect; in the catalysed reactions, the maximum temperature reached in the cleaning bath was ~ 26 °C. In the uncatalysed reaction, the temperature reached ~ 50 °C during insonation at the higher intensity but the polymerisation time was less than one-third that of a "silent" reaction at 80 °C.

Figure 2 near here.

VM10, a mixture of MDI and TDI isomers, is used in a range of polyurethane plastics. Table 1 shows the polymerisation times for this monomer with butane diol and with two poly(ethylene glycols). Again, it is noticeable that the use of ultrasound greatly speeds up the initial phase of the reaction. In commercial uses, the reaction mixture is typically poured into a mould and simply cured in an oven. To compare with the sonochemical work, reactions were also performed with vigorous mechanical stirring. This also decreases the time taken to start the polymerisation although a hard product similar to that from an oven cure was only obtained after long several hours. This suggests that the enhanced mixing of reagents caused by ultrasound is at least a contributory factor in the rate acceleration.

Table 1 near here.

Table 2 shows results for the preparation of 1,4 butane diol based polyurethanes with TMXDI and with IPDI. In each case, the reaction is faster under sonochemical conditions. Although the molecular weights produced are relatively low, the polymers produced with the assistance of ultrasound generally have somewhat higher values.

Table 2 near here.

To obtain further information on the process, the reaction of H₁₂MDI was studied in more detail. This reaction was chosen since it is widely used in commercial polyurethane formulations and also because it is complete in a relatively short time. Figure 3 shows the effect of ultrasound on polymerisations with seven diols. All reactions were started at 25 °C, the non-ultrasound reactions being agitated vigorously with a mechanical stirrer. The polymerisation time was again taken as that required for the system to gel or solidify. This was usually accompanied by a significant exotherm.

The reaction time in the absence of ultrasound increased with the viscosity of the diol. However, this was not the case when ultrasound was used. It was also noted in the reactions with the PEG's that, after the system gelled, the temperature rose to around 45 °C in the stirred reactions while in the sonochemical polymerisations > 100 °C was noted. Again, this indicates that a greater degree of reaction is occurring in the latter case.

Figure 3 near here.

The effect of increasing the ultrasound intensity is shown in Figure 4. Larger intensities indicate greater ultrasonic energy entering the system and a consequent increase in the number of cavitation bubbles and sonochemical effect. As might be expected, higher intensities lead to shorter reaction times.

Figure 4 near here.

Figure 5 shows the molecular weights of the polyurethanes formed in these experiments. As seen in the preliminary experiments, in each case the polymers produced ultrasonically have higher molecular weights. Also noteworthy was that they generally had higher polydispersities, ranging from 2.5 – 4 whereas the conventional experiments had values between 2.0 – 2.9. Similar results were seen with the other diols investigated.

Figure 5 near here.

In contrast to the polymerisation times, variation of the ultrasound intensity had little effect on the molecular weight. Reaction of H₁₂MDI with PEG 600 at five intensities between 20.3 and 40.4 gave M_n between 6000 and 7000. This may reflect that the final molecular weight achieved is dependent on the polymerisation that occurs during curing after the reaction mixture gels and so is less influenced by the ultrasound. The chain lengths obtained here are too short for the ultrasonic degradation process to take place.

Further discussion

One explanation for the enhanced reactivity would be the heating caused by sonication. However, the bulk temperature of the reaction mixture never rose to greater than ~ 50 °C and the sonochemical rates were faster than the “silent” versions at this temperature. The collapse of cavitation bubbles results in very large temperatures, sufficient to cause pyrolysis of the reacting compounds, for a microsecond or so. It may be that a small amount of material around a collapsing bubble becomes hot enough to promote the reaction, overcoming its activation energy¹. A greater effect arises from the extremely efficient mixing of the components enhanced by ultrasound.

Figure 6 investigates the possibility that the rate enhancements are due simply to the heating effect of the ultrasound. To determine the degree of this heating, an amount of PEG400 equal to the total of the reactants involved was sonicated at the highest intensity used. Also shown are the temperature rises during a stirred polymerisation and one conducted under sonication. The temperature rise in the final case is larger than that expected from the stirred reaction plus ultrasonic heating. A simple heating effect does not therefore explain the results. The higher molecular weights achieved under insonation also indicate that a greater extent of reaction has been achieved.

Figure 6 near here.

Among the chemical effects due to cavitation is the formation of radicals due to breakdown of the vapour entering the cavitation bubbles. However, this is unlikely to be an effect in these reactions. Another possibility is that the catalyst action is modified in some way. Ligand exchange processes can be promoted under insonation and the formation of compounds with unusual oxidation states has been reported¹⁸. However, considerable sonochemical rate enhancements were observed in reactions with no catalyst so that this cannot be a complete explanation.

A number of attempts were made to follow the kinetics of the polyurethane formation. However, the experimental set-up made it very difficult to achieve reproducible results. This was due to the difficulty in obtaining consistent samples from the viscous mixture when it starts to react. A number of methods including titration of the remaining isocyanate and gas chromatography were used. No convincing data could be obtained from this preliminary work and further work is underway using model compounds to overcome these difficulties. However, to illustrate the effects, Figure 7 shows infra-red spectroscopic data for the reaction of IPDI with butane diol at (initially) 25 °C. The reactions were sonicated or stirred for 30 min after which a small amount of the reacting mixture was spread onto a NaCl plate and mounted in the spectrometer. The reaction was followed by monitoring the loss of the isocyanate carbonyl peak at 2256 cm^{-1} compared with the growth of the urethane carbonyl at 1695 cm^{-1} . The reaction initiated under ultrasound still proceeds at a faster rate even though sonication is not continued.

Figure 7 near here.

Conclusions

This work has show that the rate of reaction between diols and diisocyanates can be accelerated by the use of high intensity ultrasound. The source of the effect seems to be related to local heating around collapsing cavitation bubbles together with the enhanced mass transfer caused by the fluid motion. Larger extents of reaction, evidence by longer chain lengths are found in the sonochemical reactions. The range of systems used – six diols and five isocyanates – suggests that these would be general phenomena. Increasing the ultrasound intensity lowered the reaction times but had no significant effect of the molecular weight of the polymers formed. Straightforward bicomponent reaction mixtures have been used here and it may be that sonochemical enhancement would be particularly useful in more complex, multicomponent mixtures. In particular, the ability to enhance mass transport and diffusion through the fluids may have applications in the production of foams.

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Table 1. Preparation of polyurethanes containing VM10 (uncatalysed)

Diol	Reaction Conditions	Polymerisation Time / min	Product
1,4 butane diol	Heat, 50 °C	60	Brittle material
1,4 butane diol	Heat, 80 °C	30	Brittle material
1,4 butane diol	Stir, 50 °C	10	Friable foam
1,4 butane diol	U.S., 20.1 W cm ⁻²	1	Friable foam
PEG300	Heat, 50 °C	120	Hard white polymer
PEG300	Heat, 80 °C	55	Hard white polymer
PEG300	Stir, 50 °C	10	Very viscous; hardens overnight
PEG300	U.S., 20.1 W cm ⁻²	1	Very viscous; hardens 5-10 min
PEG600	Heat, 80 °C	25	Hard, transparent material
PEG600	Stir, 50 °C	20	Very viscous; hardens overnight
PEG600	U.S., 20.1 W cm ⁻²	1	Tacky, transparent material. Hardens 5-10 min

Table 2. Preparation of polyurethanes with 1,4 butanediol

	Reaction Conditions	Catalyst	Polymerisation Time / min	M _w	γ
TMXDI	Heat, 80 °C	0.1 %	10	2700	2.6
TMXDI	Stir, 50 °C	0.1 %	12	1900	2.9
TMXDI	U.S., 20.1 W cm ⁻²	0.1 %	2.5	3000	2.1
IPDI	Heat, 80 °C	0	165		
IPDI	U.S., 20.1 W cm ⁻²	0	180		
IPDI	Heat, 50 °C	0.01	110		
IPDI	Heat, 80 °C	0.01	70	2000	2.1
IPDI	Stir, 25 °C	0.01	> 360		
IPDI	U.S., 20.1 W cm ⁻²	0.01	35	10400	2.0

CAPTIONS FOR FIGURES

Scheme 1. Structures of the diisocyanates used for polyurethane formation.

Figure 1. Schematic diagram of sonication apparatus.

Figure 2. Comparison of polymerisation times (H_{12} MDI and 1,4-Butanediol) under varying reaction conditions.

Figure 3. Comparison of polymerisation times for H_{12} MDI with various diols.

Key: EG – ethylene glycol; Di – diethylene glycol; Tri - Triethylene glycol;
PEG – polyethylene glycol with the indicated average chain length.

Figure 4. The effect of ultrasound intensity on polymerisation time for H_{12} MDI polyurethanes.

Key: as Figure 3

Figure 5. Comparison of molecular weights for H_{12} MDI polymerised with various diols.

Key: as Figure 3

Figure 6. Comparison of temperature rises during polyurethane formation.

Figure 7. Infra-Red spectroscopic monitoring of kinetics of formation of a polyurethane.

Scheme 1

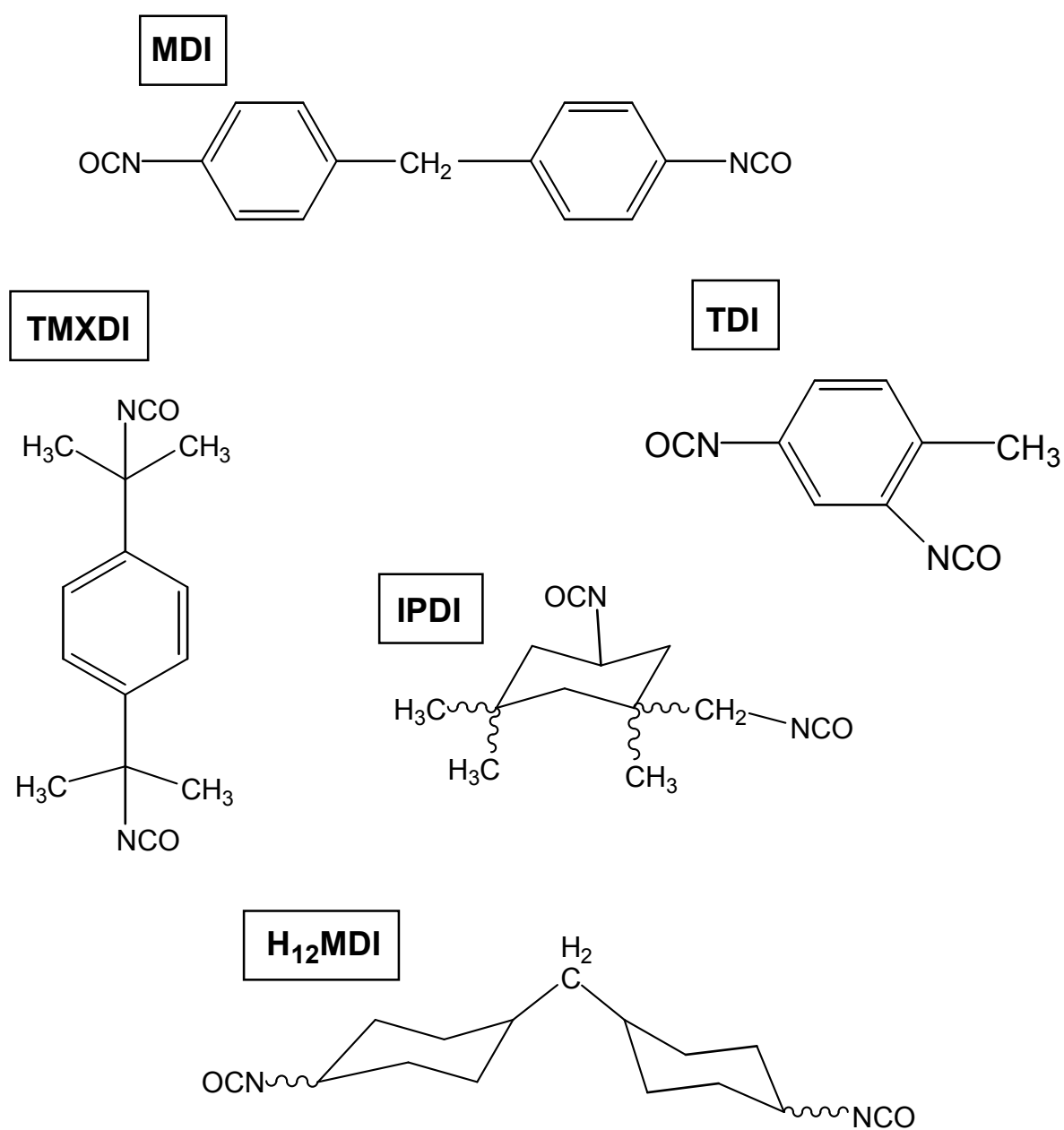


Figure 1

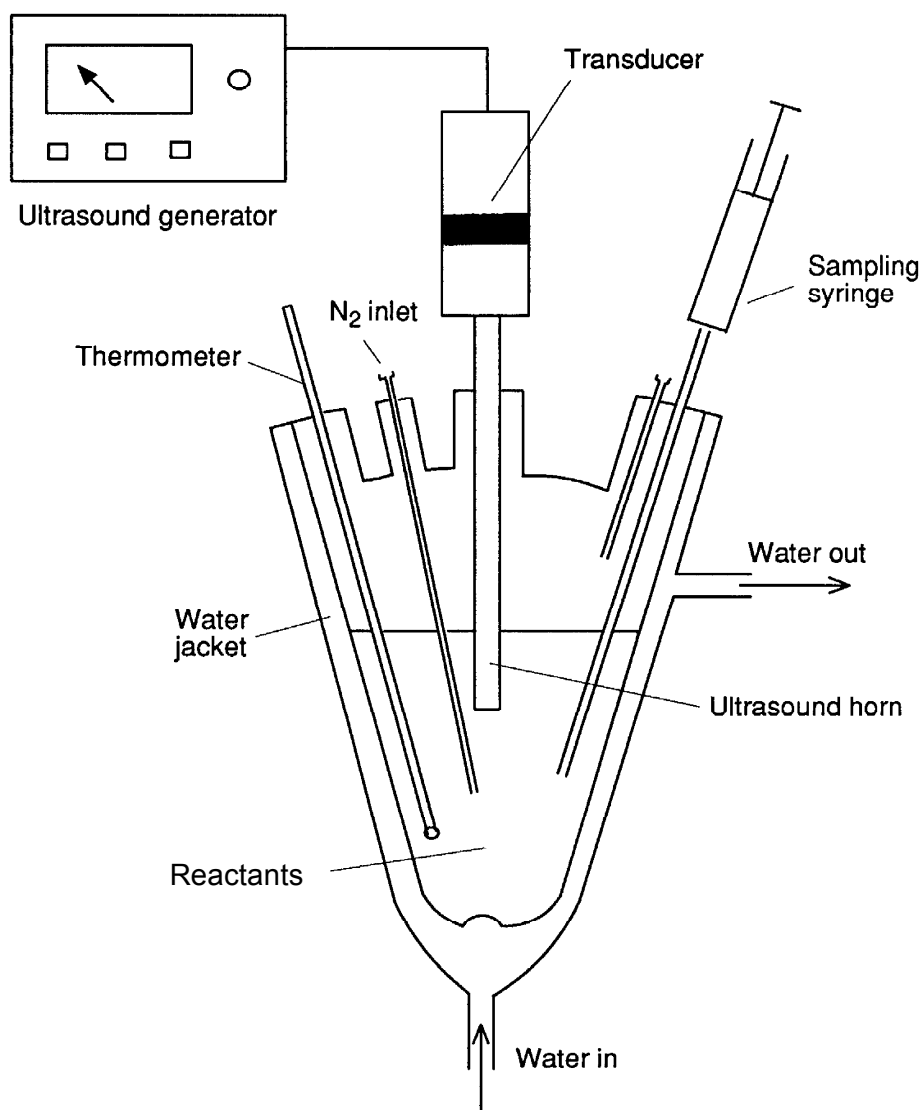


Figure 2

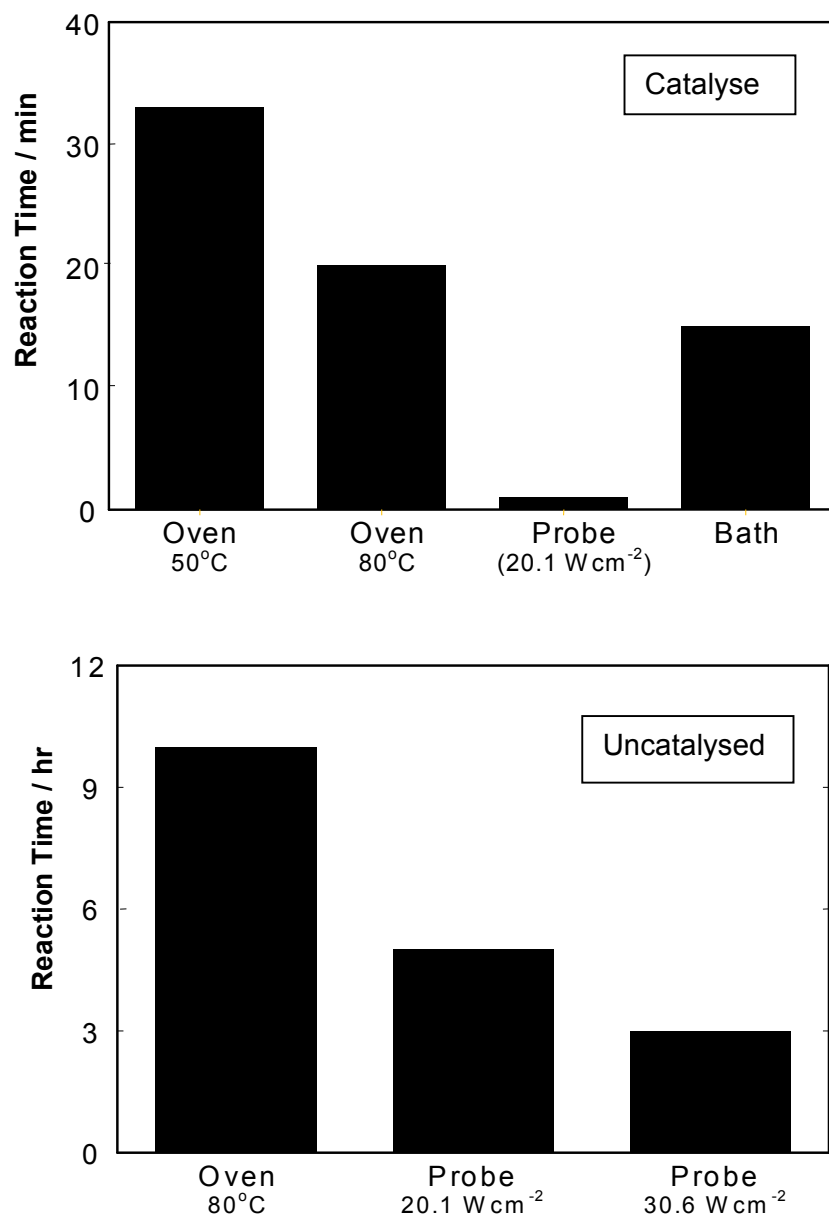


Figure 3

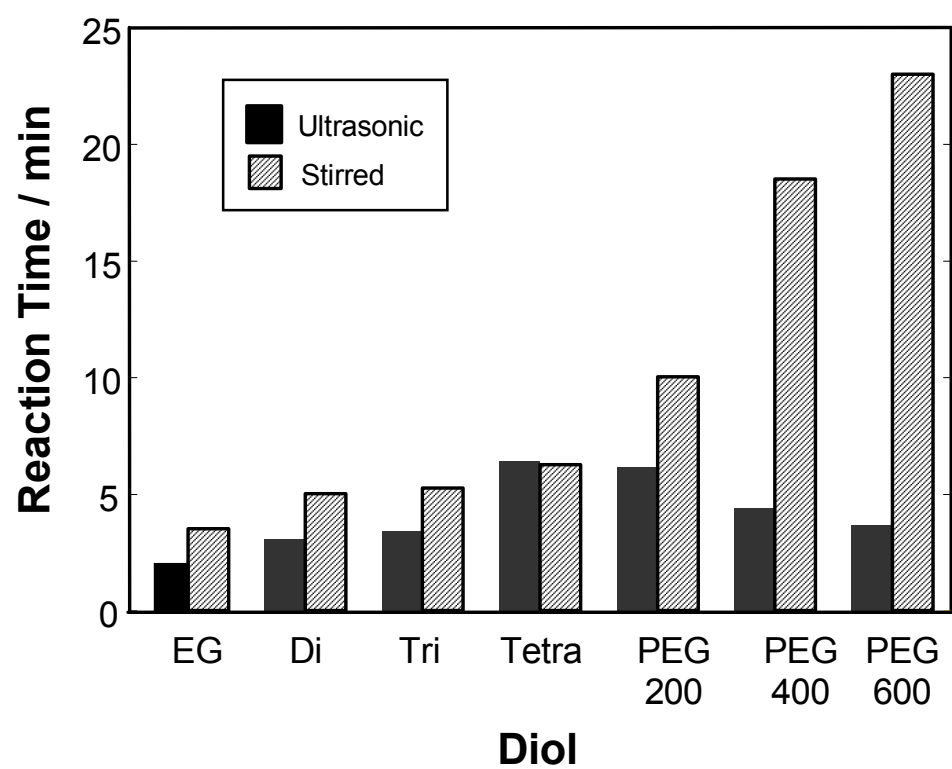


Figure 4

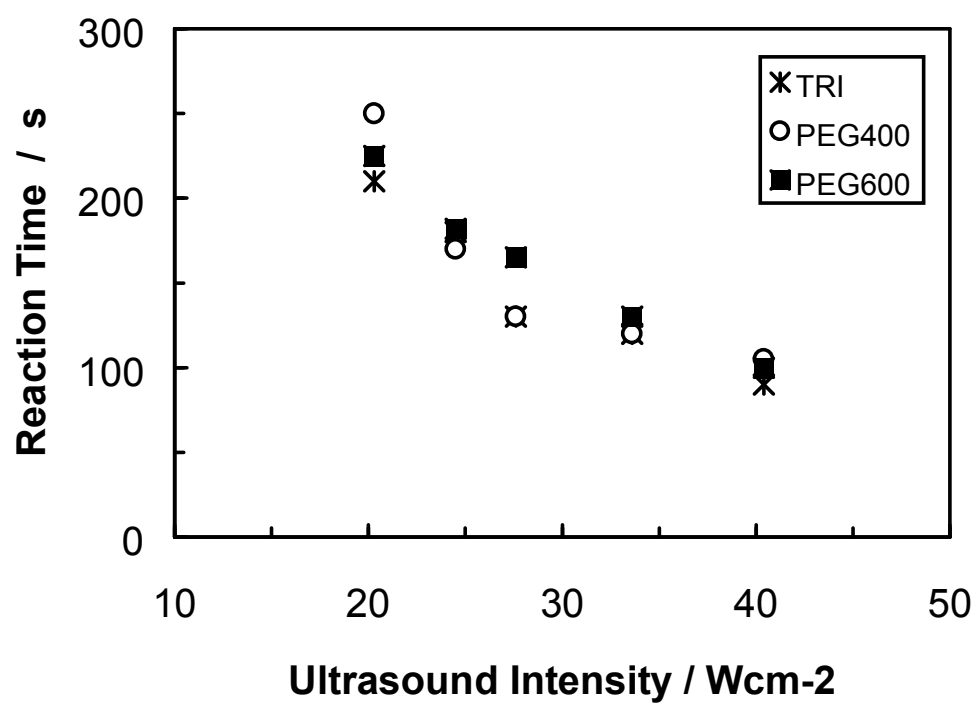


Figure 5

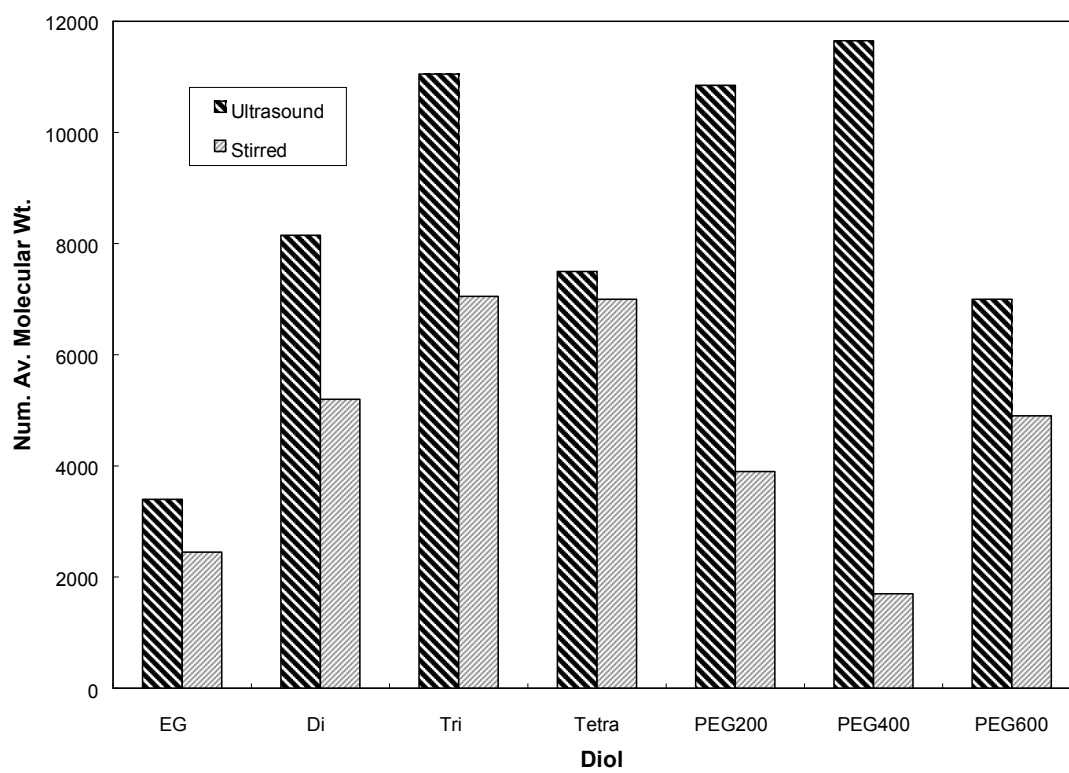


Figure 6

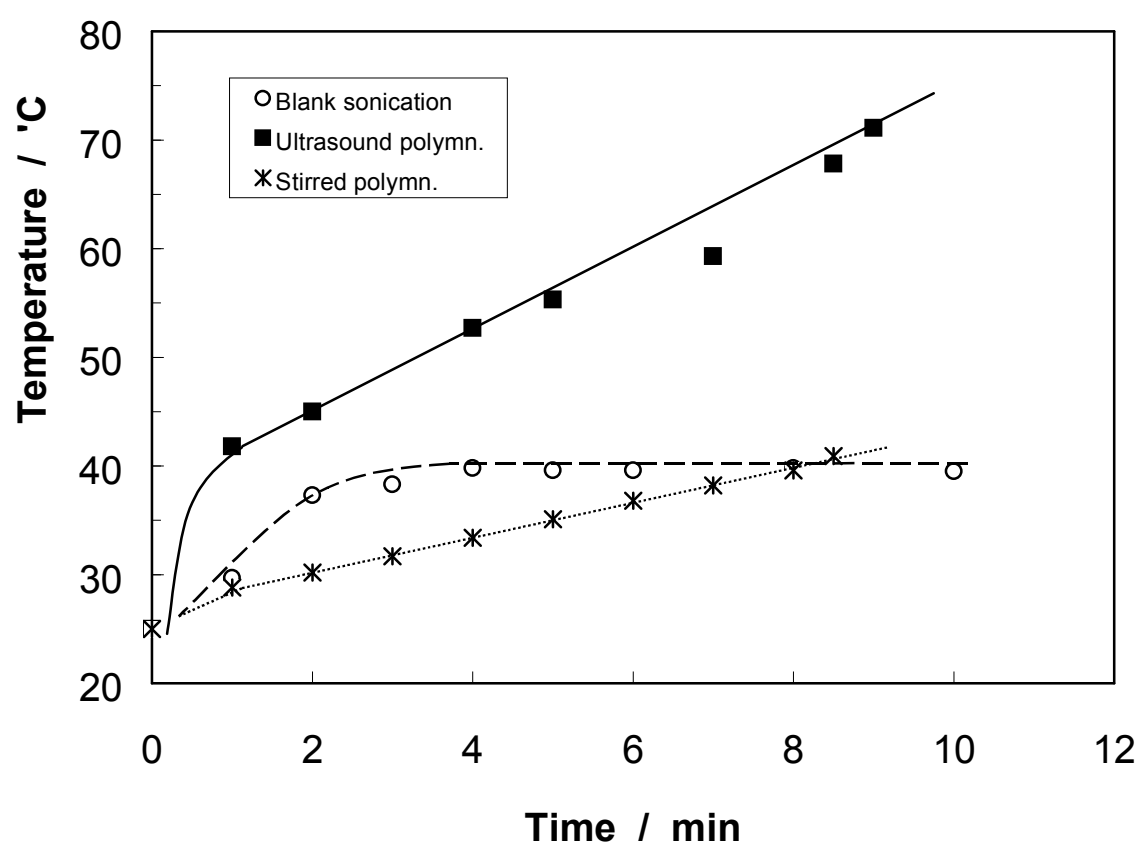


Figure 7

